Diurnal variation in the concentration of air ions of different mobility classes in a rural area

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[1] Analyzed data consist of 8900 hourly average mobility distributions measured in the mobility range of 0.00041–3.2 $cm^2\ V^{-1}\ s^{-1}$ (diameter range 0.36–79 nm) at Tahkuse Observatory, Estonia, in 1993–1994. The average diurnal variation in the concentration of cluster ions is typical for continental stations: the maximum in the early morning hours and the minimum in the afternoon. This is explained by variations in radon concentration. The diurnal variation for big cluster ions (0.5–1.3 $cm^2\ V^{-1}\ s^{-1}$) differs from that for small cluster ions (1.3–3.14 $cm^2\ V^{-1}\ s^{-1}$). The size distribution of intermediate and light large ions in the range of 1.6–22 nm is strongly affected by nucleation bursts of nanometer particles. On the burst days, the maximum concentration of intermediate ions (1.6–7.4 nm) is about the noontime and that of light large ions (7.4–22 nm) about 2 hours later. The concentration of heavy large ions (charged Aitken particles of diameters of 22–79 nm) is enhanced in the afternoon and this is explained by the bursts of nanometer particles and the subsequent growth of particles by condensation and coagulation. If the burst days are excluded, then in the warm season the concentration of Aitken particles increases during night. In the cold season, the diurnal variation is different and all the classes of aerosol ions (2.1–79 nm) show similar variation with the minimum at 0600 LT and the maximum in the afternoon; exceptions are the rare nucleation burst days. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 3304 Meteorology and Atmospheric Dynamics: Atmospheric electricity; 3307 Meteorology and Atmospheric Dynamics: Boundary layer processes; *KEYWORDS:* air ions classes, aerosol particles

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1. Introduction

[2] In the field of atmospheric electricity, the term "air ion" signifies all electrically charged airborne particles (from molecular clusters up to large aerosol particles), which serve as the carriers of electric current in the air [*Dolezalek et al.*, 1985; *Hoppel et al.*, 1986; *Tammet*, 1998a]. The average diurnal variation in air ion concentration and in air conductivity has been discussed since 1930s [*Wait and Torreson*, 1934; *Weiss and Steinmaurer*, 1937; *Hogg*, 1939; *Yunker*, 1940; *Norinder and Siksna*, 1952]. Overviews of that period can be found in the monographs [*Israël*, 1957, 1970]. Later the diurnal variation in the concentration of air ions was considered in papers [*Reinet*, 1958; *Misaki and Kanazawa*, 1969; *Prüller*, 1970; *Manes*, 1977; *Tuomi*, 1989; *Retalis et al.*, 1991; *Arold and Matisen*, 1992; *Dhanorkar and Kamra*, 1993; *Israelsson and Tammet*, 2001]. The integral Gerdien condensers were commonly applied in those measurements. The sensitivity and resolution of devices, as well as the techniques of mobility-distribution measurements were unsatisfactory in many cases [see *Israël*, 1970; *Tammet*, 1970; *Flagan*, 1998]. Often the mobility ranges of air ion classes were very wide and with quite uncertain boundaries. It was shown that the diurnal variations in air conductivity and in small air ion concentration are well correlated. Since the conductivity is mainly determined by the concentration of small air ions, the diurnal variations of these two quantities are similar. The diurnal variation in the concentration of large air ions, or charged aerosol particles, is to a greater extent affected by meteorological conditions and by local air pollution.

[3] Several models have been developed to describe the air ion balance in the atmosphere [*Israël*, 1970; *Hoppel and Frick*, 1986]. The main sources of ionization are cosmic rays, and radiation from the soil and from radioactive substances in the air. The ionization rate near the ground varies in time due to radon concentration in the air, which depends on the radon exhalation from the soil and on air mixing [*Porstendörfer*, 1994]. Free electrons and positive primary ions are generated in equal quantities by ionizing radiation. "Cluster ions" (small air ions) are formed in a charged state and evolved via ion-molecule reactions in the atmosphere before they obtain their final size [*Viggiano*, 1993; *Luts*, 1998; *Nagato and Ogawa*, 1998]. The mobility distribution (also called the mobility spectrum) of cluster

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Table 1. Classification of Air Ions[a]

Class of Air Ions	Mobility Range, $cm^2\ V^{-1}\ s^{-1}$	Diameter Range,[b] nm	Traditional Name	Class of Particles
Small cluster ions	1.3–3.2	0.36–0.85	small ions	clusters
Big cluster ions	0.5–1.3	0.85–1.6		
Intermediate ions	0.034–0.5	1.6–7.4	intermediate ions	nanometer particles
Light large ions	0.0042–0.034	7.4–22	large ions	coarse nanometer (or ultrafine) particles
Heavy large ions	0.00087–0.0042	22–79	large ions or Langevin ions	Aitken particles

[a]Corresponding classes of aerosol particles are presented in the last column.
[b]Estimates of equivalent diameter ranges assume single-charged particles.

ions is dependent on the chemical composition of the air; therefore it is also affected by photochemical processes in the atmosphere. Two concurrent processes, recombination and adsorption to aerosol particles, are responsible for the depletion of cluster ions. The adsorption to aerosol particles produces charged aerosol particles or large air ions. Thus the concentration of large air ions and that of aerosol particles should be closely correlated.

[4] Owing to the complexity and large-scale variability of atmospheric processes, the long-term measurements of air ions in a wide range of mobility are necessary to draw statistically founded conclusions about the air ion characteristics. This was the main argument for the installation of wide-range automated multichannel mobility spectrometers at Tahkuse Observatory in 1988 [*Hõrrak et al.*, 1994]. So far, the problems of the ''bursts'' of intermediate ions (generation of charged nanometer aerosol particles driven by photochemistry and boundary layer meteorology) and of the classification of air ions have been studied especially on the basis of regular measurements at Tahkuse Observatory [*Hõrrak et al.*, 1998b, 2000]. The present paper deals with the average diurnal variations of different air ion classes.

[5] A statistical analysis revealed that the entire mobility distribution (mobility spectrum) of air ions can be divided into two main classes: ''cluster ions'' with mobilities above 0.5 $cm^2\ V^{-1}\ s^{-1}$ and ''aerosol ions'' (charged aerosol particles) with mobilities below 0.5 $cm^2\ V^{-1}\ s^{-1}$ [*Hõrrak et al.*, 2000]. These two classes can in turn be divided into five almost independent air ion classes according to Table 1.

[6] Since the concentrations of ultrafine aerosol particles and their charged fraction (air ions) are closely correlated in the size range of 3–80 nm in weakly polluted rural air, the information obtained from air ion mobility distribution measurements could contribute to the study of atmospheric aerosols [*Hõrrak et al.*, 1998a, 1998c; *Tamm et al.*, 2001; *Mäkelä et al.*, 2001].

2. Measurements

[7] The measurements of air ion mobility distributions were carried out at Tahkuse Observatory (58°31′N 24°56′E), which is located in a sparsely populated rural region, 27 km northeast of the city of Pärnu and 100 km south of Tallinn, the capital of Estonia. Pärnu, with 52,000 inhabitants, is on the coast of the Gulf of Riga, on the east coast of the Baltic Sea.

[8] A complex of air ion spectrometers covering a mobility range of 0.00041–3.14 $cm^2\ V^{-1}\ s^{-1}$ was installed at Tahkuse Observatory in 1988 [*Hõrrak et al.*, 1994, 2000; *Hõrrak*, 2001]. The complex consists of three original multichannel aspiration spectrometers designed according to the principle of the second-order differential mobility analyzer [*Tammet*, 1970]. The whole mobility range was logarithmically divided into 20 intervals: 9 intervals in the subrange of 0.00041–0.29 $cm^2\ V^{-1}\ s^{-1}$ and 11 intervals in the subrange of 0.25–3.14 $cm^2\ V^{-1}\ s^{-1}$. The recorded air ion mobility fractions and the estimated equivalent diameter ranges are presented in Table 2. The equivalent diameters were calculated assuming single-charged particles [*Tammet*, 1995, 1998b]. Five classes of air ions established by means of statistical analysis are also given. By convention, the spectrometers are called the small ion spectrometer (IS_1), the intermediate ion spectrometer (IS_2), and the large ion spectrometer (IS_3). Thus each mobility distribution consists of 20 fraction concentrations of negative (N_k) and positive (P_k) polarity.

[9] The air was sucked into the mobility spectrometers through an opening in the south gable of a farmhouse at a height of about 5 m from the ground. The air intake is shielded from the atmospheric electric field by tall trees surrounding the building. Details about the environment and

Table 2. Air Ion Fractions of Negative (N_k) and Positive (P_k) Polarity, Estimates of Equivalent Diameter Ranges Assuming Single-Charged Particles, and Proposed Classes of Air Ions

Analyzer	Fraction	Mobility, $cm^2\ V^{-1}\ s^{-1}$	Diameter, nm
		Small Cluster Ions	
IS_1	N_1/P_1	2.51–3.14	0.36–0.45
IS_1	N_2/P_2	2.01–2.51	0.45–0.56
IS_1	N_3/P_3	1.60–2.01	0.56–0.70
IS_1	N_4/P_4	1.28–1.60	0.70–0.85
		Big Cluster Ions	
IS_1	N_5/P_5	1.02–1.28	0.85–1.03
IS_1	N_6/P_6	0.79–1.02	1.03–1.24
IS_1	N_7/P_7	0.63–0.79	1.24–1.42
IS_1	N_8/P_8	0.50–0.63	1.42–1.60
		Intermediate Ions	
IS_1	N_9/P_9	0.40–0.50	1.6–1.8
IS_1	N_{10}/P_{10}	0.32–0.40	1.8–2.0
IS_1	N_{11}/P_{11}	0.25–0.32	2.0–2.3
IS_2	N_{12}/P_{12}	0.150–0.293	2.1–3.2
IS_2	N_{13}/P_{13}	0.074–0.150	3.2–4.8
IS_2	N_{14}/P_{14}	0.034–0.074	4.8–7.4
		Light Large Ions	
IS_2	N_{15}/P_{15}	0.016–0.034	7.4–11.0
IS_3	N_{16}/P_{16}	0.0091–0.0205	9.7–14.8
IS_3	N_{17}/P_{17}	0.0042–0.0091	15–22
		Heavy Large Ions	
IS_3	N_{18}/P_{18}	0.00192–0.00420	22–34
IS_3	N_{19}/P_{19}	0.00087–0.00192	34–52
IS_3	N_{20}/P_{20}	0.00041–0.00087	52–79

the instrumentation are given by *Hõrrak et al.* [2000] and *Hõrrak* [2001].

[10] The hourly averages and standard deviations of air ion fraction concentrations of negative and positive polarity inside the hourly periods were recorded together with the values of meteorological parameters and the concentration of NO_2. The main data set for this paper consists of about 8900 hourly average mobility distributions collected during 14 months from 1 September 1993 to 27 October 1994.

3. Results and Discussion

3.1. Cluster Air Ions

[11] The average diurnal variation in the concentration of cluster ions (0.5–3.2 $cm^2\ V^{-1}\ s^{-1}$) for the entire period had the ordinary shape for continental stations: the maximum in the early morning hours at 0600–0700 LT was $n_- = 270\ cm^{-3}$ and $n_+ = 303\ cm^{-3}$ and the minimum in the evening at 1800 LT was $n_- = 222\ cm^{-3}$ and $n_+ = 247\ cm^{-3}$, for the ions of negative and positive polarity, respectively. Examining the diurnal variations in the cluster ion concentration calculated for individual months, contrasts became apparent. In the cold season (from October 1993 to April 1994 and October 1994), when the soil was frozen and covered by snow or it was wet, the diurnal variation was weakly expressed, and the average concentration was relatively low (see Figure 1). In the warm season (September 1993, and from May to September 1994), when the soil was dry and unfrozen, the average concentration was higher and the average diurnal variation was of larger extent; only June 1994 was an exception, without a significant diurnal variation. The diurnal variation of negative small ions was close to that of positive ions; the ratio of positive to negative ion concentration (coefficient of unipolarity) was 1.11 and 1.15 in the warm and cold season, respectively. The lack of considerable electrode effect can be explained by the relatively high position (5 m) of air inlet and the screening of the electric field by trees surrounding the building where the instrumentation is located [*Hõrrak et al.*, 2000].

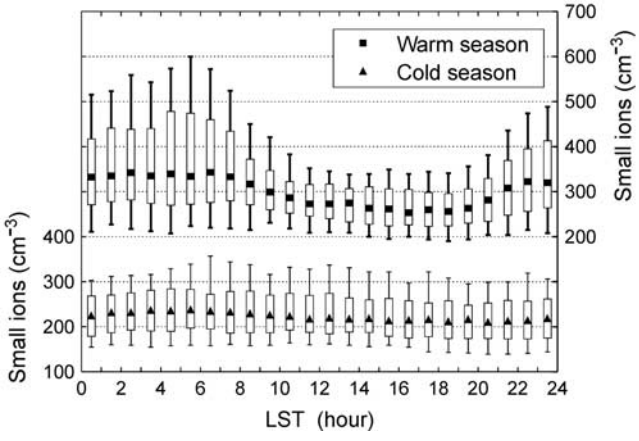

Figure 1. Average diurnal variation in the concentration of positive cluster ions (mobility 0.5–3.14 $cm^2\ V^{-1}\ s^{-1}$) in the warm season (September 1993 and May–September 1994) and in the cold season (November 1993–April 1994). Statistics: median, box (25 and 75%), and whiskers (10 and 90% quantiles).

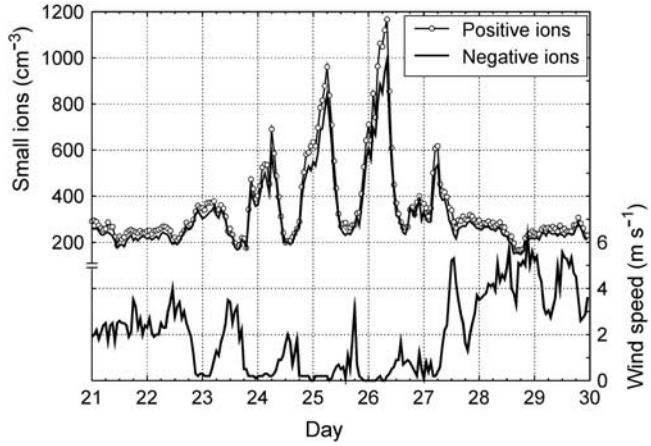

Figure 2. Diurnal variation in the concentration of cluster ions (0.5–3.14 $cm^2\ V^{-1}\ s^{-1}$) and wind speed from 21 to 30 August 1994.

[12] In the warm season, the concentration of cluster ions has the average diurnal variation of a single waveshape with the maximum in the nighttime and the minimum in the afternoon, as it was for the entire period. The highest concentrations were recorded in fine weather conditions during anticyclones in July and August. The absolute maximum of cluster ions recorded on 26 August was 996 cm^{-3} for negative ions and 1176 cm^{-3} for positive ions, both in the early morning hours at 0800–0900 LT (Figure 2). The cause of the high concentrations was probably the accumulation of radon near the ground during nocturnal calms. The daytime minimum values of about 240 cm^{-3} for negative ions and 270 cm^{-3} for positive ions were close to the background concentrations. The highest peaks were recorded at the end of a 3-day period of very weak winds at the daytime and calm in the nighttime (Figure 2).

[13] All the months with a considerable diurnal variation in cluster ion concentration (from May to September, except June) were also characterized by a significant diurnal variation in wind speed (also in air temperature and relative humidity) and by very weak wind or calm at the nighttime. The monthly diurnal variation in the concentration of cluster ions distinctly varied in the same phase as the changes in relative humidity and in the opposite phase to air temperature and wind speed. In July, when all these quantities had a regular diurnal variation of large extent (drought period), the correlation coefficients of the cluster ion hourly average concentrations with air temperature, relative humidity, and wind speed were −58, 59, and −59%, respectively. The known effect of radon on the ionization rate of the air controlled by the convective and turbulent exchange of the air near the ground played a key role for the observed correlations. The diurnal variation in the concentration of aerosol particles in the Aitken mode range of 22–79 nm (interpreted by the heavy large ion concentration) was nearly parallel to that of cluster ions. The relatively low percentage of nocturnal calms in June was obviously the main cause of the weak diurnal variation in cluster ion concentration.

[14] In the cold season, the diurnal variation in the median concentration of cluster ions was very weak of

about 30 cm^{-3} (Figure 1). The maximum of negative ions was about 210 cm^{-3} (positive ions 240 cm^{-3}) at 0500–0600 LT and the minimum 180 cm^{-3} (210 cm^{-3}) at about 2000 LT. The average diurnal variation of cluster ions showed an opposite correlation with that of heavy large ions (see Figure 7a) and was therefore probably caused by the variation in the aerosol particle content in the air. Sometimes, the enhancement of cluster ions by about 100–200 cm^{-3} was observed, but most of them correlated negatively with the heavy large ion concentration.

[15] Measurements at Tahkuse in August and September 1998 showed a clear diurnal variation in radon activity concentration in fine weather, from about 2–3 Bq m^{-3} in the afternoon up to 25 Bq m^{-3} in the early morning hours during calms. On other days the activity concentration of radon was in the range of about 4–6 Bq m^{-3}. The concentration of cluster ions was found to be dependent on both the concentrations of radon and aerosol particles (mainly of the diameters of 50–300 nm). The diurnal variation in the radon concentration depending on the stability of boundary layer air is well known [*Porstendörfer*, 1994; *Raunemaa et al.*, 1996; *Kataoka et al.*, 1998]. The development of an ionization profile (ion concentration at different heights below 2 m) during quiet summer nights at Uppsala was studied by *Norinder and Siksna* [1952].

[16] The diurnal variation of cluster ions at Tahkuse in 1985–1986 had a low secondary afternoon peak, especially in autumn [*Hõrrak et al.*, 1988]. The present measurements showed that the secondary afternoon peak of cluster ions (in October) correlated oppositely with the concentration of heavy large ions (charged Aitken particles).

[17] *Dhanorkar and Kamra* [1993] have reported the average diurnal variation of small ions at a height of 1 m above the ground at a tropical land station in Pune, India, in 1990–1991. The concentration minima in the afternoon of about 200–400 cm^{-3} were comparable considering all the seasons, the maxima in the early morning hours varied in the range of 1000–5000 cm^{-3}. The measurements of air conductivity at Helsinki-Vantaa Airport, Finland, in 1977–1986 [*Tuomi*, 1989] and at Marsta Observatory, Sweden, in 1993–1998 [*Israelsson and Tammet*, 2001] showed higher amplitudes of the diurnal variation (with a maximum in the nighttime) in summer than in winter. The average conductivity at Helsinki-Vantaa Airport was about 40% higher and at Marsta Observatory 7 times higher than at Tahkuse. The differences could originate from the different heights of measurement points and from the peculiarities of soil properties (e.g., the content of radioactive substances, porosity), which result in differences in the ionization rate of the air close to the ground. The measurements in the center of Athens for 1968–1980 [*Retalis et al.*, 1991] resulted in a double oscillation diurnal variation in conductivity, and the average conductivity was about 2 times lower than at Tahkuse. The origin of these differences obviously lies in differences between the urban and rural environment.

[18] The detailed analysis of the narrow mobility fractions of cluster ions (0.5–3.14 $cm^2\ V^{-1}\ s^{-1}$) showed that it is rational to classify cluster ions into two groups called small and big cluster ions, respectively [*Hõrrak et al.*, 2000]. These groups showed a different shape of the diurnal variation in the concentration. Negative cluster ions with the natural mean mobility and standard deviation of 1.53 ± 0.10 $cm^2\ V^{-1}\ s^{-1}$ (positive ions of 1.36 ± 0.06 $cm^2\ V^{-1}\ s^{-1}$) were classified into groups with the boundary at 1.3 $cm^2\ V^{-1}\ s^{-1}$ (1.0 $cm^2\ V^{-1}\ s^{-1}$).

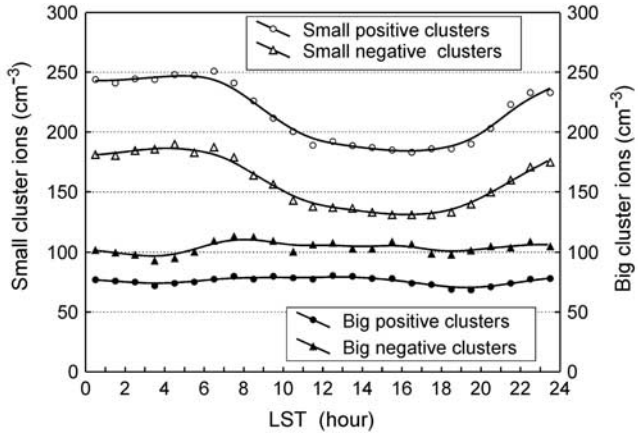

Figure 3. Diurnal variation in the median concentration of positive and negative small cluster ions and big cluster ions in the warm season (September 1993, May–September 1994).

[19] In the warm season, the average diurnal variation in cluster ion concentration was mainly caused by small cluster ions (Figure 3).

[20] The diurnal variation in big cluster ions was weak in general and showed different behavior in different months. For example, during the first decade of September 1993, after the inflow of cool and clean marine Arctic air masses, the concentration of big cluster ions of negative polarity showed a regular diurnal variation (nearly opposite to that of small cluster ions) with the maximum of the median concentration at the daytime at about 1500 LT and the minimum in the early morning hours at 0400 LT. The diurnal variation of positive big cluster ions was less pronounced. Also in June, the median concentrations of small and big cluster ions exhibited moderate nearly opposite diurnal variations, and therefore the variation in the total concentration of cluster ions disappeared. The minimum of the median concentration of big cluster ions in June was also recorded in the early morning at 0400 LT.

[21] In July the median concentrations of small cluster ions of both polarities showed the diurnal variation with large extent of about 200 cm^{-3} (most likely due to the effect of radon to the ionization rate of air). Nevertheless, the median concentrations of big cluster ions were relatively steady of about 100 cm^{-3}, showing a little variation (about 30–40 cm^{-3}) of similar shape with the diurnal variation of small cluster ions. The enhancement of the hourly average concentration of big cluster ions by 50–100 cm^{-3} was recorded during the nocturnal calms when the concentration of small cluster ions rose above 300 cm^{-3}, but no clear correlation between the absolute values was noticed.

[22] The mobility distribution of cluster ions (0.5–3.2 $cm^2\ V^{-1}\ s^{-1}$) is affected by the nucleation bursts (detected by the concentration of intermediate ions); during the burst the changes take place mainly in the low-mobility wing of the distribution (below 1 $cm^2\ V^{-1}\ s^{-1}$). The bursts coincide with the minima of the mean mobility of cluster

ions in the diurnal cycle [*Hõrrak et al.*, 1998b]. Considering the days with the nucleation bursts in the warm season, the diurnal variation in the concentration of small cluster ions showed a common single oscillation, but the big cluster ions showed a double oscillation: one maximum recorded at midnight and the secondary maximum at noon. The minimum in early morning hours at 0500 LT coincides with the air temperature and absolute humidity minima and the relative humidity maximum; the secondary minimum was recorded at 1900 LT.

[23] In the cold season, the general shape of the diurnal variation of small cluster ions was similar to that in the total concentration of cluster ions in Figure 1. The concentration of big cluster ions was nearly constant at about 50 cm^{-3}. During the bursts of intermediate ions, negative big cluster ions showed a peak median concentration of about 100 cm^{-3} and positive cluster ions of 80 cm^{-3} at noontime.

[24] We suppose that the changes in the mobility distribution of cluster ions (proportion of small and big cluster ion concentration) are due to the changes in the chemical composition and concentration of some trace gases or vapors in the air, probably generated by photochemical reactions. The distribution is also affected by the ionization rate and by the concentration of aerosol particles, which have an effect on the lifetime of cluster ions. The variation in the proportion of small and big cluster ion concentration during the diurnal cycle causes a diurnal variation in the mean mobility of cluster ions.

[25] The different behavior of cluster ions above 1 cm^2 V^{-1} s^{-1} (called molions) and of the total concentration of small ions in the urban atmosphere in Tartu, Estonia during 1951 and 1960–1963 has also been discussed by *Reinet* [1958], *Marran* [1958], and *Prüller* [1970].

3.2. Intermediate Ions

[26] The size distribution of aerosol ions is strongly affected by photochemical nucleation bursts occurring occasionally around noon in specific meteorological conditions [*Hõrrak et al.*, 1998b; *Clement et al.*, 2001], e.g., after the inflow of clean marine Arctic air masses in spring and in fall. The photochemical nucleation can initiate a burst of intermediate ions (charged aerosol particles in the size range of 1.6–7.4 nm) and the subsequent evolution of the size distribution of aerosol ions below 80 nm. The generated new aerosol particles grow toward the sizes of 10–15 nm during 2–3 hours. In general, the disturbed region of air ion size distribution affected by the bursts is 1.1–34 nm (0.002–1.0 cm^2 V^{-1} s^{-1}) including the groups of big cluster ions, nanometer particles, and a fraction of Aitken particles. Figure 4 presents an example of the subsequent evolution of aerosol ions toward large sizes. Hereinafter, the diurnal variations of different classes of aerosol ions (intermediate, light large, and heavy large ions) are analyzed considering the nucleation bursts and nonburst situations. A day is classified as a "burst day" if the concentration of intermediate ions (diameter 1.6–7.4 nm) exceeds 100 cm^{-3} during at least 2 hours; the opposite case is called a "nonburst day."

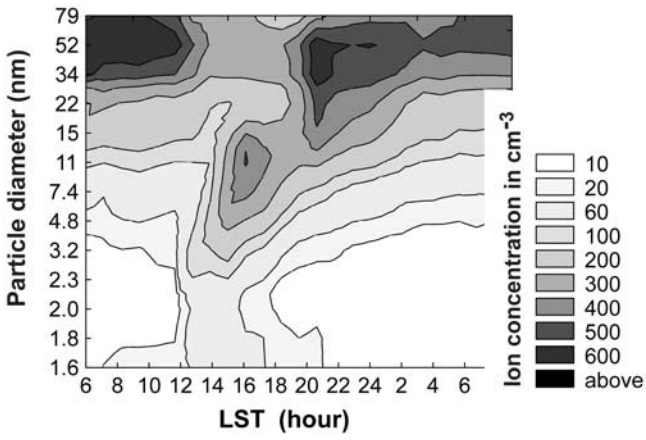

Figure 4. Contour plot of the evolution of aerosol ion size distribution at Tahkuse on 20 October 1994.

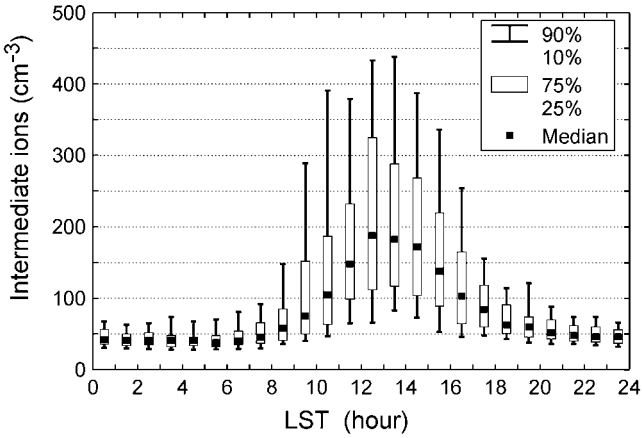

Figure 5. Diurnal variation in the concentration of positive intermediate ions (mobility 0.034–0.5 cm^2 V^{-1} s^{-1}; diameter 1.6–7.4 nm) considering the days with the bursts of intermediate ions. September 1993–October 1994. Statistics: median, box (25 and 75%), and whiskers (10 and 90% quantiles).

[27] The average diurnal variation in the concentration of intermediate ions (mobility 0.034–0.50 cm^2 V^{-1} s^{-1}; diameter 1.6–7.4 nm) calculated for the whole measurement period had one peak value at local noontime [*Hõrrak et al.*, 1998b]. The median concentrations of negative and positive ions were quite steady about 50 cm^{-3}. Considering only the days with the bursts of intermediate ions more than 100 cm^{-3}, the diurnal variation in the median concentration also became evident (see Figure 5). The median concentration (also higher quantiles) of negative intermediate ions had higher amplitude of diurnal variation with the maximum of 224 cm^{-3} at noon compared to that of positive ions of 186 cm^{-3}. The enhanced median concentrations recorded from 0900 to 1800 LT are in accordance with the typical duration of bursts from 6 to 9 hours.

[28] During the evolution of aerosol ion mobility distributions, the median concentrations of narrow mobility fractions of 0.034–0.32 cm^2 V^{-1} s^{-1} reached their peak values at different times at about local noontime. The lower is the mobility of the fraction, the later occurs the time of the peak value.

[29] The diurnal variation presented in Figure 5 was characteristic of the anticyclonic weather and was probably initiated by a photochemical nucleation process that started

Table 3. Diurnal Variations in the Medians of Meteorological Parameters Recorded During the Burst/Nonburst Days[a]

Time LT, Hours	Temperature, °C	Relative Humidity, %	Absolute Humidity, g m^{-3}	Wind Speed, m s^{-1}
4–5	1.3/6.5	94/94	4.9/6.8	1.1/1.4
14–15	12.1/13.5	43/66	4.9/7.7	3.0/2.6

[a]1 September–16 November 1993 and 25 February–27 October 1994.

at sunrise and achieved the maximum intensity at noon. The generation of intermediate ions followed after sunrise, with a delay of about 2–3 hours, during the stage of quick development of the boundary layer. Thus the formation of intermediate ions was closely related to the boundary layer meteorology. The median concentration of intermediate ions was correlated negatively with the median relative humidity and positively with the median air temperature and wind speed during diurnal cycle. The correlation coefficients are −89, 91, and 85%, respectively (critical coefficient at confidence 95% is about 40%).

[30] The bursts occurred on sunny days, when the solar radiation was intense, the temperature difference between early morning and afternoon was large, and relative humidity decreased significantly from morning to noon. The main differences between the meteorological parameters during the burst days and nonburst days are presented in Table 3.

[31] It was characteristic of bursts, especially of very high bursts, that the rise in concentration was more abrupt than the decrease to the background concentration. Sometimes very sharp bursts were recorded when the peak concentration was reached within 1 hour (the time resolution of the data was 1 hour). Some of them showed a clear correlation with the passage of fronts. For example, on 30 April 1994 at 1000–1100 LT, the concentration of intermediate ions increased suddenly to about 860 cm^{-3} and then gradually decreased to background concentration of about 40 cm^{-3} during the following 5–6 hours.

[32] Observations of intermediate ions at Tahkuse showed the behavior similar to that of nanometer aerosol particles [*Weber et al.*, 1995, 1997; *McGovern et al.*, 1996a, 1996b; *Birmili and Wiedensohler*, 2000]. The nanoparticle formation events were detected at the Hyytiälä SMEAR station in southern Finland [*Mäkelä et al.*, 1997, 2000a, 2000b; *Kulmala et al.*, 1998; *Aalto et al.*, 2001] after a change from the stable stratification of atmosphere at night to mixing in the morning hours at 0800–0900 LT, with the concentration maximum around noon. The nanoparticles with the measured sizes of about 3 nm grew during 6–12 hours, reaching the Aitken size range of 60–70 nm in the evening. The effects of air masses, synoptic weather, and boundary layer evolution on aerosol formation are discussed in detail by *Nilsson et al.* [2001a, 2001b].

[33] The diurnal variation of intermediate ion concentration of different character was observed at a tropical land station by *Dhanorkar and Kamra* [1992, 1993]. The concentration of intermediate ions was measured by means of two Gerdien ion counters with the critical mobilities of 0.02 and 0.75 cm^2 V^{-1} s^{-1}; the corresponding size of particles was about 1.3–9.8 nm. In transition and monsoon periods, the concentration of intermediate ions at a height of 1 m above the ground showed a maximum after sunrise between 0600 and 0900 LT. Afterward, with a delay of about 1–3 hours after sunrise, it suddenly dropped. In winter and summer, the concentration of intermediate ions, as well as that of large ions, increased steadily thorough the night and decreased after sunrise.

3.3. Light Large Ions

[34] The light large ions (mobility 0.0042–0.034 cm^2 V^{-1} s^{-1}; diameter 7.4–22 nm) varied differently from intermediate ions; their maximum concentrations were shifted to somewhat later hours. In the case of the bursts of intermediate ions an evolution process was observed in the range of intermediate and light large ions; the distribution peak shifted from smaller diameters to larger ones [*Hõrrak et al.*, 1998b]. In contrast to the intermediate ions, no significant difference between the negative and positive light large ion concentrations was observed.

[35] To distinguish the possible influence of photochemical nucleation bursts on the diurnal variation of light large ions from other mechanisms of gas-to-particle conversion, two different situations have been examined: burst days and nonburst days. The contrast of diurnal variations in Figure 6 is apparent. A lot of new particles, produced by the nucleation bursts, grew by the condensation and coagulation, showing a peak concentration in the size range of light large ions of

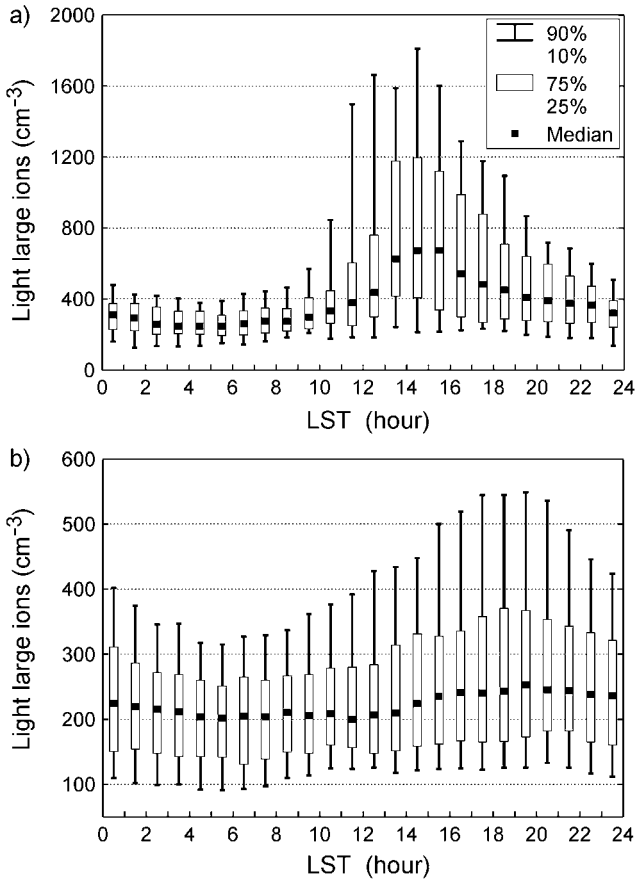

Figure 6. Diurnal variation in the concentration of positive light large ions (0.0042–0.034 cm^2 V^{-1} s^{-1}; 7.4–22 nm) (a) considering the days with the bursts of intermediate ions and (b) without bursts. September 1993–October 1994. Statistics: median, box (25 and 75%), and whiskers (10 and 90% quantiles).

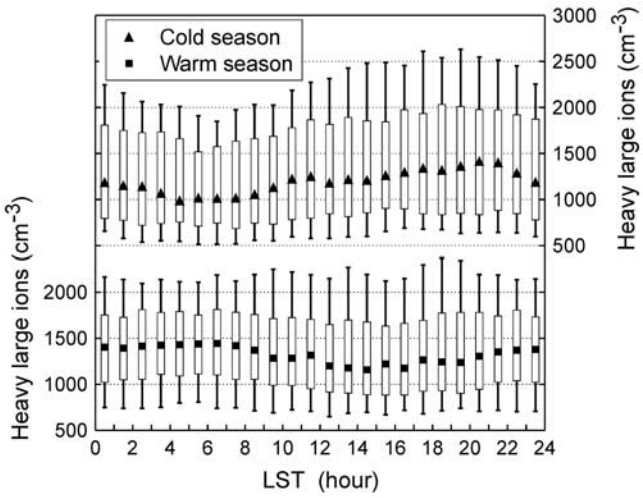

Figure 7. Diurnal variation in the concentration of positive heavy large ions (0.00041–0.0042 $cm^2\ V^{-1}\ s^{-1}$; 22–79 nm) in the cold season (November–March) and in the warm season (May–September). Statistics: median, box (25 and 75%), and whiskers (10 and 90% quantiles).

7.4–22 nm in the afternoon. The rate of particle production by other mechanisms was weaker, and the maximum concentrations were shifted to later hours in the evening. Stable atmosphere in the evening could favor the process.

[36] The decrease in the median concentration of light large ions (as well as 75 and 90% quantile) during the nighttime was characteristic to all the months. It was probably due to the coagulation and growth by the condensation of these particles into large ones; also the removal from the atmosphere by deposition could be significant [*Hoppel et al.*, 1990]. In the wintertime, the minimum appeared at 0600 LT, but in other months a secondary minimum was recorded at noontime (considering the nonburst days). The minimum at noon (about 200 cm^{-3}) became dominant in July and August (drought period). In contrast to this, the average concentration in the afternoon displayed a high maximum of about 850 cm^{-3} in May. The high bursts of intermediate ions in May and the absence of them in July and August could explain the contrast in the light large ion concentrations.

[37] *Ulevičius et al.* [1991] have measured aerosol particle size distributions in the range of 20–500 nm at the Aisetas background station in Lithuania (100 km NE from Vilnius, about 370 km SSE from Tahkuse) during summers in 1986–1987. Three types of distributions were distinguished according to the directions of long-range transport: across the Baltic Sea, from the unpolluted northern regions, and from the industrial regions of Western Europe. All the cases showed a distinct diurnal variation in the concentration of ultrafine particles of the diameter of about 30 nm during the anticyclonic weather. The first had a peak in the afternoon, the second in the evening; the third type was a combination of the first two. No clearly expressed diurnal variations were registered during cyclonic weather.

3.4. Heavy Large Air Ions (Charged Aitken Particles)

[38] The average diurnal variation in the concentration of heavy large ions or charged Aitken particles (mobilities 0.00041–0.0042 $cm^2\ V^{-1}\ s^{-1}$; diameters 22–79 nm) was very weak, in general. Considering the cold and warm season separately, the diurnal variations displayed different behavior (Figure 7). In the cold season, the minimum of the median concentration of about 1000 cm^{-3} was recorded in the early morning hours at 0600 LT and the maximum of 1420 cm^{-3} in the late evening at 2000–2100 LT. In the warm season, the early morning hours at 0600–0700 LT exhibited the concentration maximum of about 1440 cm^{-3}; the minimum of 1170 cm^{-3} was recorded in the afternoon at 1400–1500 LT. The diurnal variation in the median concentration was modest (about 300–400 cm^{-3}) compared with the overall statistical average and the standard deviation of 1190 ± 700 and 1330 ± 620 cm^{-3} for the cold and warm season, respectively. The diurnal variations of negative and positive heavy large ions were closely correlated.

[39] In the warm season, the diurnal variation in the median concentration of heavy large ions depicted in Figure 7 was characteristic to all of the months from June to September (May was an exception, probably due to the high bursts of intermediate ions). It was more clearly expressed in the conditions of very hot and durable anticyclones in July 1994 (drought period). A peculiarity for these months was the relatively high amplitude of the diurnal variation in meteorological parameters, and weak wind or calm in the nighttime (see Table 4). The diurnal variation in the median concentration of heavy large ions correlated positively with the median relative humidity (correlation coefficient was 96%, the critical coefficient at confidence 95% was about 40%) and oppositely with air temperature (−96%) and wind speed (−94%).

[40] In the warm season, the diurnal variation in large ion concentration could be well explained by the accumulation of aerosol particles close to the ground during nocturnal inversions and by the changes in the stability of the boundary layer in the morning. The formation of particles during the nighttime was probably due to the gas-to-particle conversion based on radiolytic processes. The latter was supposed because, in the warm season, the diurnal variation in the median concentration of heavy large ions in Figure 7 showed a similarity to that of cluster ions in Figure 1. The nearly parallel diurnal variations of small and large ions were found also by *Arold and Matisen* [1992] and *Dhanorkar and Kamra* [1993]. A simultaneous enhancement of cluster ion and heavy large ion concentrations during nighttime was sometimes recorded at Tahkuse. For example, in July, during the period of about 2 weeks, the correlation coefficient between the concentrations of cluster and heavy large ions was 62 and 48% for positive and negative polarity, respectively.

[41] The ability of ionizing radiation to produce besides cluster ions also condensation nuclei (Aitken particles) in the presence of some trace gaseous species in the air is well

Table 4. Diurnal Variations in the Medians of Meteorological Parameters During the Cold/Warm Season[a]

Time LT, Hours	Temperature, °C	Relative Humidity, %	Absolute Humidity, g m^{-3}	Wind Speed, m s^{-1}
5–6/4–5	−5.0/8.8	92/94	3.1/8.0	2.4/0.5
14–15	−2.3/18.7	81/49	3.3/9.0	3.1/2.4

[a]Cold season: November–March; warm season: May–September.

known [e.g., *Vohra et al.*, 1970; *Hopke and Ramamurthi*, 1988; *Ramamurthi et al.*, 1993]. The details of the process, concerning atmospheric aerosol production, are currently a point of issue.

[42] Despite the apparent regularity of the average diurnal variation in the heavy large ion concentration in the cold season (Figure 7), we have to notice that it is a long-term statistical average. Considering different months from November to March, the minima of the median concentrations were recorded in the early morning hours at about 0500–0700 LT; the maxima took place at different times in the evening. A secondary maximum around noon was recorded in February and March. Because of the high variability of the monthly median concentrations of heavy large ions in the cold season (most probably due to the variation in monthly precipitation), a large database (about 3 months) was necessary to obtain a clear pattern of diurnal variations.

[43] In winter, the diurnal variation in the median concentration of heavy large ions was similar to that of light large ions. All the groups of aerosol ions (mobility 0.00041–0.29 $cm^2\ V^{-1}\ s^{-1}$; diameter 2.1–79 nm) showed the diurnal variation of a similar shape, if to exclude the days with the bursts of intermediate ions. As the aerosol ions of both polarities showed the same regularities, only the average concentrations are shown in Figure 8.

[44] The concentration of intermediate ions in Figure 8a showed a maximum before the heavy large ions reached the maximum in the evening. The decrease in the concentration during the nighttime was probably due to deposition, coagulation, and growth of particles by condensation. The cause of the particle generation, which started in the early morning, remained indistinct. In winter, the NO_2 correlated with the concentration of heavy large ions; the correlation coefficients were in the range of 54–77% from November to February, and 41% in March. Probably, the combustion of fuels influenced the diurnal variation of large ions, as well as the entire group of aerosol ions during the heating period. However, only a weak and roughly similar diurnal variation in the median concentration of NO_2 was found: the minimum of about 3.2 $\mu g\ m^{-3}$ was at 0500–0600 LT and the maximum 4 $\mu g\ m^{-3}$ at 2100–2200 LT.

[45] The diurnal variations in the median concentrations of aerosol ion classes in the warm season (from May to September), excluding the days with the bursts of intermediate ions are presented in Figure 8b. In comparison with the cold season, all the aerosol ion classes showed a different behavior. The amplitude of the diurnal variation in the intermediate ion concentration is very low, but the variation of the nanometer particles, which they represent, is many times larger. The bipolar charging probabilities for the existence of a single elementary charge (of one polarity) on the particles of the diameters of 2.1, 7.4, 22, and 79 nm are about 0.7, 3.8, 12, and 24%, respectively [*Reischl et al.*, 1996].

[46] The diurnal variation in the median concentration of heavy large ions in the warm season is generally opposite to that in the cold season. The diurnal variation of meteorological parameters in the cold season was of low amplitude compared with the warm season (Table 4). We suppose that the differences in the mixing of the boundary layer air and different processes of aerosol particle generation (combustion versus radiolytic processes) could explain the contrast

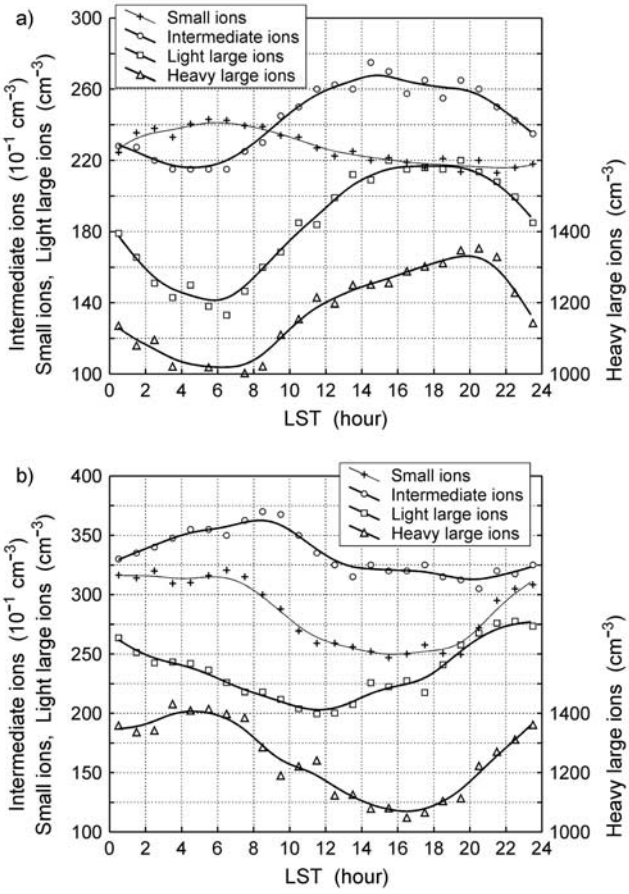

Figure 8. Diurnal variation in the median concentration of positive cluster ions (0.5–3.14 $cm^2\ V^{-1}\ s^{-1}$), intermediate ions (2.1–7.4 nm), light large ions (7.4–22 nm), and heavy large ions (22–79 nm) (a) in the cold season (November–March) and (b) in the warm season (May–September), excluding the days with the bursts of intermediate ions.

of the diurnal variations in heavy large ion concentration in the cold and warm seasons. Also, the influence of the local air pollution is more pronounced in winter, when the thickness of vertically mixed atmospheric boundary layer is about 300 m, compared to 1.5–2 km in summer.

[47] *Juozaitis et al.* [1996] measured the continental aerosol particle size distributions in summer 1990 and winter 1992 at the Aisetas station and in a suburb of Vilnius, Lithuania. The condensation of low-pressure vapors formed by the gas-phase chemical reactions was found to be the predominant mechanism of the growth of aerosol particles smaller than 120 nm through the whole year. The particles smaller than 50 nm had different growth rates in winter and in summer, because of their different nature. In the cold season, a considerable amount of aerosol particles with diameters below 50 nm (about 60% of 20 nm) were hydrophobic and obviously originated from combustion processes.

[48] One particular problem that can be studied on the basis of the diurnal variations is how the nucleation bursts of nanometer particles (intermediate ions) contribute to the heavy large ion concentration (charged Aitken particles) [*Hõrrak et al.*, 2001]. It is rather complicated to draw

reasonable conclusions when examining single burst events at a single measuring point (Eulerian experiment). In general, the disturbed region of air ion size distributions affected by the bursts is from 1.1 to 34 nm (0.002–1.0 cm^2 V^{-1} s^{-1}). The gradual shift of the distribution peak beyond 22 nm was observed only sometimes in the case of intensive burst events. However, the diurnal variations presented by *Mäkelä et al.* [2000a] often showed a clear growth of nanometer aerosol particles up to the Aitken mode or even to the accumulation mode size range (up to 200 nm) in spring. The advection of air masses, turbulent and convective mixing, and various processes that affect the Aitken particle concentration in the air [*Hoppel et al.*, 1990; *Seinfeld and Pandis*, 1998] can blur the effect. Also, the factors that determine the peculiarities of the nucleation process (e.g., the surface concentration of preexisting particles) could be different. The monitoring of ultrafine aerosol formation at widely spaced stations showed that the nucleation events may occur almost simultaneously over hundreds up to a thousand kilometers during the same cold air outbreak from the Arctic [*Mäkelä et al.*, 1998; *Vana et al.*, 2000; *Nilsson et al.*, 2001a].

[49] A statistically weighty database of the bursts obtained for the warm season from May to September (57 days when the concentration of intermediate ions exceeded 100 cm^{-3}) enables to study the influence of the bursts of intermediate ions on the heavy large ion concentration in more detail. The diurnal variations in the heavy large ion concentration during the days with the bursts of intermediate ions versus common (nonburst) situations are presented in Figure 9. Considering the nonburst days, the median concentration of intermediate ions was relatively steady of about 32–37 cm^{-3} (see Figure 8). The diurnal variations of the basic meteorological parameters are presented in Table 5.

[50] We assume that the average diurnal variation in the concentration of heavy large ions (charged Aitken particles) during the nonburst days was caused by the mixing of the air close to the ground at daytime and by the particle generation of a different mechanism than during the nucleation bursts. Considering the burst events, the relatively higher concentration of charged Aitken particles in the afternoon was probably caused by the bursts of nanometer particles and the subsequent growth of particles by condensation and coagulation toward large sizes. The boundary layer mixing in the afternoon was likely comparable in both cases. Both cases showed an increase in the Aitken particle, as well as in the cluster ion concentration during the nighttime, probably due to radiolytic processes (initiated by ^{222}Rn and ^{220}Rn decay) favored in the conditions of nocturnal calms. The diurnal variation in the concentration of cluster ions in the burst days was similar to that in the nonburst days (see Figure 8b), but the concentration median was higher by about 12–16% during the peak time of the bursts from 1000 to 1500 LT and by about 6–7% during the rest of the day.

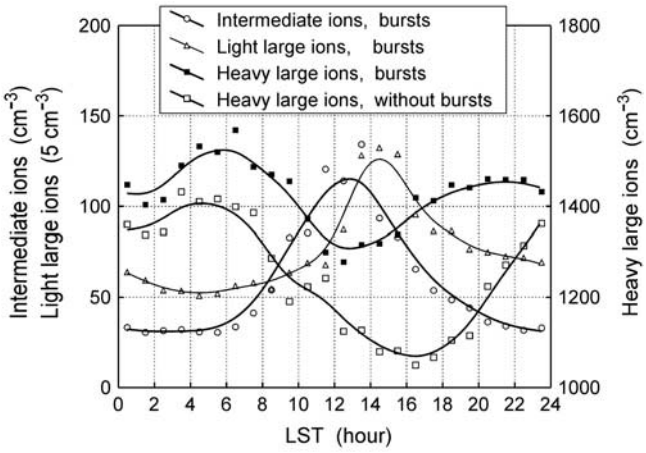

Figure 9. Diurnal variation in the median concentration of intermediate ions (diameter 2.1–7.4 nm), light large ions (7.4–22 nm), and heavy large ions (22–79 nm) in the warm season (the burst events of intermediate ions versus common situation). September 1993, May–September 1994.

Table 5. Diurnal Variations in the Medians of Meteorological Parameters Recorded During the Burst/Nonburst Days in the Warm Season (September 1993, May–September 1994)[a]

Time LT, Hours	Temperature, °C	Relative Humidity, %	Absolute Humidity, g m^{-3}	Wind Speed, m s^{-1}
4–5	5.7/10.6	94/93	6.4/8.9	0.5/0.4
13–14/14–15	18.8/19.3	43/56	6.5/10.3	2.6/2.1

[a]Median wind speed maxima around 1600 LT were 3.0/2.2 m s^{-1}.

[51] During the cold season, the background concentration of heavy large ions was rather variable and the number of burst events was not sufficient to draw statistically grounded conclusions about the contribution of the bursts of nanometer particles (intermediate ions) to the heavy large ion concentration.

4. Conclusions

[52] The average diurnal variation in the concentration of cluster ions at Tahkuse was typical for continental stations with the maximum in the early morning hours and the minimum in the afternoon. The diurnal variation was distinctly developed in the warm season and weakly developed in the cold season when the soil was wet or it was frozen and covered by snow. The results are in accordance with the hypothesis that radon is the main ionizing agent, which causes the variation in the ionization rate, and therefore in the concentration of cluster ions near the ground.

[53] Cluster ions (0.5–3.14 cm^2 V^{-1} s^{-1}) are divided into two subclasses of small and big cluster ions with the boundary at 1.3 cm^2 V^{-1} s^{-1} for negative ions and 1.0 cm^2 V^{-1} s^{-1} for positive ions. The diurnal variation of the concentration of small cluster ions is similar to the variation of the entire group of cluster ions. The diurnal variation in the concentration of big cluster ions is weak and sometimes even in opposite phase compared to that of small cluster ions. Considering the days with the nucleation bursts of nanometer particles (intermediate ions), the diurnal variation in the concentration of big cluster ions showed the maximum at noon; in the warm season the second maximum was recorded near midnight.

[54] The diurnal variation in the concentration of intermediate and light large ions with the diameters of 1.6–22 nm is strongly affected by the photochemical nucleation bursts of

nanometer aerosol particles in favorable meteorological conditions. In the burst days, the maximum in the concentration of intermediate ions (1.6–7.4 nm) was found about the noontime. The light large ions (7.4–22 nm) varied differently from intermediate ions; their maximum concentration was shifted and occurred a few hours later. In the case of nucleation bursts an evolution process was observed in the range of intermediate and light large ions: the distribution peak shifted from smaller diameters to larger ones.

[55] The average diurnal variation in the concentration of heavy large ions (charged Aitken particles) with the diameters of 22–79 nm was usually weak. Considering the cold and warm seasons separately, the diurnal variations displayed different behavior. If the rare nucleation events were excluded, then in the cold season all the classes of aerosol ions (2.1–79 nm) showed similar diurnal variation with the minimum at 0600 LT. The concentration of intermediate ions exhibits the maximum in the afternoon, before the heavy large ions reach the maximum in the evening around 2000 LT; a decrease during nighttime is probably due to deposition, coagulation, and growth of particles by condensation.

[56] In the warm season, the concentration of heavy large ions (charged Aitken particles of 22–79 nm in diameter) increases during the nighttime, probably due to radiolytic processes favored in the conditions of nocturnal calms, and it reaches the maximum at 0600–0700 LT, gradually decreasing later up to about 1700 LT. In the days with nucleation bursts the concentration of heavy large ions was enhanced in the afternoon compared with the nonburst days. This is explained as a consequence of the particle evolution (growth) toward large sizes.

[57] In the cold season the diurnal variation in the concentration of heavy large ions is nearly in the opposite phase to that in the warm season. This contrast can be explained by the different processes of aerosol particle generation (combustion versus radiolytic processes). In winter the concentrations of charged Aitken particles and NO_2 were positively correlated (the correlation coefficients were 41–77%).

[58] Variation of different classes of air ions provides information about different processes in the atmosphere, e.g., accumulation of radon near the ground depending on the stability of boundary layer, generation and growth of nanometer particles during nucleation bursts, and changes in Aitken particle concentration.

[59] **Acknowledgments.** This research has in part been supported by the Estonian Science Foundation through grant 4622.

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